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13. ABSTRACT *(Maximum 200 words)*

Semi-empirical configuration interaction (SECI) theory has been extended to predict activation barriers for combustion reactions of boron group halide oxidation reactions. Good agreement with experiments has been obtained. Rate coefficients for BO oxidation reactions have been measured. It is shown that these reactions, as well as their AlO equivalents, proceed through formation of intermediate complexes. The CO Fourth Positive System chemiluminescence in the vacuum ultraviolet has been studied in two reaction systems: $O + C_2H_2$ and $C_2 + O_2$. The latter is shown to be more likely responsible for rocket plume emissions.

14. SUBJECT TERMS
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Research Objectives

The reporting period of this AASERT grant overlapped with that of consecutive parent grants. For one of these the goal was to provide accurate kinetic data on, and further develop predicitve techniques for, metallic species reactions from combustion of advanced solid propellants, including HEDMs (high-energy density materials). Under the other we study chemiluminescent reactions for rocket plume detection. The work done by the AASERT students consequently has addressed both aspects.

Results and Publications

The progress made is best described by the publications resulting from the grant. These are, with abstracts:

1. **Alan S. Blue, David P. Belyung, and Arthur Fontijn, "Activation Barriers for Series of Exothermic Homogoous Reactions, V. Boron Group Diatomic Species Reactions", The Journal of Chemical Physics, 107, 3791-3796 (1997).**

Semiempirical configuration interaction (SECI) theory is used to predict activation barriers E, as defined by $k(T) = AT^n \exp(-E/RT)$. Previously SECI has been applied to homologous series of oxidation reactions of s^1, s^2, and s^2p^1 metal atoms. Here it is extended to oxidation reactions of diatomic molecules containing one s^2p^1 atom. E values are calculated for the reactions of BH, BF, BCl, AlF, AlCl, AlBr, GaF, GaI, InCl, InBr, InI, TlF, TlCl, TlBr, and TlI with O_2, CO_2, SO_2, or N_2O. These values correlate with the sums of ionization potentials and Σ-Π promotion energies of the former minus the election affinities of the latter. In the earlier work n was chosen somewhat arbitrarily, which affected the absolute values of E. Here it is shown that examination of available experimental and theoretical results allows determination of the best values of n. Using this approach yields n=1.9 for the present series. For the seven reactions, which have been studied experimentally, the average deviation of the SECI activation barrier prediction from experiment is 4.0 kJ mol^{-1}. Energy barriers are calculated for another 52 reactions.

2. **David P. Belyung, George T. Dalakos, John-David R. Rocha, and Arthur Fontijn, "Wide-Temperature Range Kinetics of the BO Reactions with O_2, HCl, and CO_2. Comparison to AlO Reactions", 27th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, in press.**

Rate coefficients for the title BO reactions have been measured by using laser-induced fluorescence in high-temperature reactors. The results obtained are, for BO + $O_2 \rightarrow$ BO_2 + O (1) k(298 - 960 K) = 7.9 x 10^{-12} exp(161 K/T) and for BO + HCl $\rightarrow$ products (2) k(293 - 760 K) = 6.3 x 10^{-13} exp(-1403 K/T), both in units of cm^3 $molecule^{-1}$ s^{-1}. Upper limits are found for BO + $CO_2 \rightarrow$ products (3). Reactions (1) and (2) have pre-exponentials two orders of magnitude smaller than the corresponding AlO reactions. Evidence is presented suggesting that all six reactions proceed through complexes, which for BO are thought to readily dissociate back to the reactants. This would explain why reaction (3) is too slow for observation. That reaction, and its reverse, were considered as very sensitive in models for B/O/H/C system combustion.

3. **Athur Fontijn, Mai Y. Randall, Abdellatif Goumri, and Paul E. Brock II, "Comparison of Mechanisms Leading to CO Fourth Positive System Vacuum Ultraviolet Chemiluminescence", AIAA Paper 98-3538.**

The kinetics of reactions leading to the $CO(A^1\Pi\text{-}X^1\Sigma)$ Fourth Positive vacuum ultraviolet emission is studied for incorporation in plume radiation models. A fast-flow reactor and a high-temperature, pseudo-static, photochemistry reactor have been used. Experiments with the former on the O + C_2H_2 reaction have shown that the intensity of the $CO(d^3\Delta\text{-}a^3\Pi)$ Triplet bands decreases with increasing pressure. This is in accord with the proposed mechanism for $CO(A^1\Pi)$ formation, by collision-induced curve crossing from CO triplet states. Experiments in the pseudo-static reactor have confirmed the increase of the $CO(A^1\Pi\text{-}X^1\Sigma)$ chemiluminescence intensity with pressure, as indicated by this mechanism, but show a decrease in the intensity of the emission when the C_2 + O_2 reaction is investigated instead. This indicates a direct $CO(A^1\Pi)$ formation in the latter reaction, which leads to more intense vuv emission and may be a more important reaction for rocket exhausts. As the first step toward obtaining the absolute light intensities and chemiluminescence efficiencies for the C_2 + O_2 reaction, its vuv emission is used to obtain its overall rate coefficients, k(300-976 K) = 1.8×10^{-11} exp (-451 K/T) cm^3 $molecule^{-1}$ s^{-1}. These values are in excellent agreement with earlier experiments, where the C_2 consumption rate coefficients were measured instead.

Students Supported by this Grant

The following U.S. citizen students have been supported:

1. Alan S. Blue, who is continuing work towards the Ph.D. degree.

2. David P. Belyung, who received his Ph.D. in Chemical Engineering in May 1997. Thesis title:" "Kinetics of Metal Combustion Reactions".

3. George T. Dalakos, who received his M.S. in Chemical Engineering in May 1996. Thesis Title: BO Reactions over a Wide Temperature Range"

4. John-David R. Rocha, who left the program without completing a degree.

5. Mai Y. Randall, who has completed her work and is currently writing her M.S. thesis.

6. Paul E. Brock II, who participated in the work as an Undergraduate Research Assistant.